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PART XIV

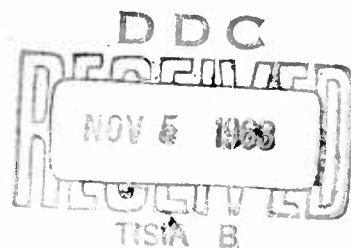
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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XIV. HIGH TEMPERATURE VAPORIZATION STUDIES

TECHNICAL DOCUMENTARY REPORT No. WADD 60-782
PART XIV

SEPTEMBER 1963



AF MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS DIVISION
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF 61(052)-225 by the
Universite Libre de Bruxelles, Brussels, Belgium;
J. Drowart)

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FOREWORD

This report was prepared by the University of Brussels, Belgium under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Deputy Commander/Research and Engineering, Aero-nautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

This report covers work done from July 1962 to July 1963.

ABSTRACT

A brief summary of the mass spectrometric technique used to obtain thermochemical information at high temperatures is given, as well as data for a number of elements, alloys chalcogenides and carbides.

This technical documentary report has been reviewed and is approved.



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INTRODUCTION

The present report summarizes work done during the past one and a half years at the Laboratoire de Chimie Physique Moléculaire, University of Brussels. It presents definite results for a number of systems and preliminary ones for others still under investigation.

The mass spectrometer^(1,2) and experimental technique have been described previously^(3,4). Briefly, obtaining thermochemical data is based upon the evaporation of the sample from a Knudsen cell of known temperature, formation of a molecular beam, ionization of the neutral species by electron impact with electrons of adjustable energy (5-70 ev) and identification of the parent molecules from the mass, appearance potential and ionization efficiency curves of the ions. Pressures P_i are obtained for the various molecules so identified through pressure

calibrations based on quantitative evaporations of known amounts of the sample or of pressure calibrants, or on the observation of known equilibria. The first procedure requires in general knowledge of the relative ionization cross sections of species of minor importance. The second procedure requires this knowledge for all species, including the pressure calibrant. These cross sections are either measured by simultaneous or successive quantitative evaporations of the sample and of a reference element, the study of congruently vaporizing compounds^(5,6) or the use of double oven techniques^(7,10), or derived from calculated values⁽¹¹⁾. Heats of reaction ΔH_0° are calculated from the relations

$$\Delta H_0^\circ = \Delta F_T^\circ - T \Delta((F_T^\circ - H_0^\circ)/T)$$

or $\Delta H_T^\circ = -R d \ln K / d(1/T)$

where $\Delta F_T^\circ = -RT \ln K$ is the change in free energy,

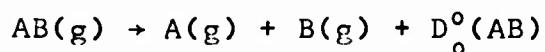
$K = \prod_i P_i^{v_i}$ the equilibrium constant,

v_i the stoichiometric coefficient for each reactant or product in the reaction considered,

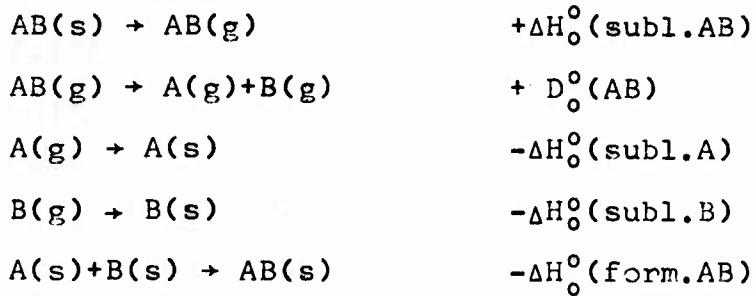
$\Delta((F_T^\circ - H_0^\circ)/T)$ the difference in free energy function of products and reactants,

T the absolute temperature.

Dissociation energies D_0° given below were obtained either directly from equilibria of the type



or from thermochemical cycles



The systems studied comprise elements, alloys, carbides, oxides, sulfides, selenides and tellurides. The results obtained are as follows:

Reaction	ΔH_0^0 or D_0^0 in kcal/mole	ref.
1. Elements		
$B(s) \rightarrow B(g)$	128.0 ± 2.5	12
$B_2(g) \rightarrow 2B(g)$	65.5 ± 5.5	12
$S_2(g) \rightarrow 2S(g)$	97.2 ± 5	13,14
(obtained in the study of CaS, SrS and BaS) (see 5)		
$Se_2(g) \rightarrow 2Se(g)$	77.2 ± 5	14
(obtained in the study of ZnSe (see 9)		
2. Alloys.		
$AgSn(g) \rightarrow Ag(g) + Sn(g)$	31.6 ± 5	15
$CuSn(g) \rightarrow Cu(g) + Sn(g)$	41.4 ± 4	15
$AuSn(g) \rightarrow Au(g) + Sn(g)$	57.5 ± 4	15
$AuCr(g) \rightarrow Au(g) + Cr(g)$	50.4 ± 3.5	16
$AuPd(g) \rightarrow Au(g) + Pd(g)$	33.3 ± 5	15

3. Systems Boron-Carbon and Boron-Carbon-Silicon.

$1/4B_4C(s) \rightarrow B(g) + 1/4C(\text{graphite})$	131.5 \pm 2.5	12
$BC(g) \rightarrow B(g) + C(g)$	105 \pm 10	17
$B_2C(g) \rightarrow 2B(g) + C(g)$	260 \pm 10	17
$BC_2(g) \rightarrow B(g) + 2C(g)$	302 \pm 10	17
$BSi(g) \rightarrow B(g) + Si(g)$	70 \pm 10	17
$BCSi(g) \rightarrow B(g) + C(g) + Si(g)$	250 \pm 10	17

4. Magnesium, Calcium and Strontium oxides (G. Verhaegen and G. Exsteen) (Molybdenum or Tungsten crucibles).

$MgO(g) \rightarrow Mg(g) + O(g)$	77 \pm 10
$CaO(g) \rightarrow Ca(g) + O(g)$	97 \pm 6
$SrO(g) \rightarrow Sr(g) + O(g)$	97 \pm 6
$Sr_2O(g) \rightarrow 2Sr(g) + O(g)$	180 \pm 12
$SrMoO_3(g) \rightarrow SrO(g) + MoO_2(g)$	150 \pm 20
$SrMoO_4(g) \rightarrow SrO(g) + MoO_3(g)$	175 \pm 20
$SrWO_3(g) \rightarrow SrO(g) + WO_2(g)$	160 \pm 20
$SrWO_4(g) \rightarrow SrO(g) + WO_3(g)$	190 \pm 20

5. Calcium, Strontium, Barium and Manganese Sulfides.

$CaS(s) \rightarrow CaS(g)$	142.8 \pm 5 (298°K)	13,14
$CaS(g) \rightarrow Ca(g) + S(g)$	71.0 \pm 5	13,14
$SrS(s) \rightarrow SrS(g)$	136.2 \pm 12 (298°K)	14
$SrS(g) \rightarrow Sr(g) + S(g)$	73.9 \pm 5	14

$\text{BaS(s)} \rightarrow \text{BaS(g)}$	119	$\pm 11(298^\circ\text{K})$	14
$\text{BaS(g)} \rightarrow \text{Ba(g)} + \text{S(g)}$	90.2 ± 6		14
$2\text{BaS(s)} \rightarrow \text{Ba}_2\text{S}_2(\text{g})$	154	$\pm 16(298^\circ\text{K})$	14
$\text{Ba}_2\text{S}_2(\text{g}) \rightarrow 2\text{BaS(g)}$	84	± 11	14
$\text{MnS(g)} \rightarrow \text{Mn(g)} + \text{S(g)}$	65	± 5	18

6. Mixtures of Calcium, Strontium and Barium Oxides and Sulfides.

$\text{SO(g)} \rightarrow \text{S(g)} + \text{O(g)}$	123	± 7	14
$\text{CaO(g)} \rightarrow \text{Ca(g)} + \text{O(g)}$	100.1 ± 7		14
$\text{SrO(g)} \rightarrow \text{Sr(g)} + \text{O(g)}$	102.4 ± 10		14
$\text{BaO(g)} \rightarrow \text{Ba(g)} + \text{O(g)}$	123.0 ± 10		14

7. Indium Sulfides (R. Colin).

$\text{In}_2\text{S(g)} \rightarrow 2\text{In(g)} + \text{S(g)}$	150.0 ± 5
$\text{InS(g)} \rightarrow \text{In(g)} + \text{S(g)}$	68.5 ± 4
$\text{In}_2\text{S}_2(\text{g}) \rightarrow \text{In}_2\text{S(g)} + 1/2\text{S}_2(\text{g})$	37.2 ± 6

8. Group IV-Group VI Compounds (R. Colin, F. Degrève, J.C. Lievin, J. Michelet and G. Verhaegen).

$n/2\text{Ge(s)} + n/2\text{GeO}_2(\text{s}) \rightarrow (\text{GeO})_n(\text{g})$	56.9 ± 3 (n=1; 298°K)
	48.8 ± 5 (n=2; 298°K)
	98.5 ± 10 (n=3; 298°K)
$\text{GeO(g)} \rightarrow \text{Ge(g)} + \text{O(g)}$	156.6 ± 3
$n/2\text{Sn(s)} + n/2\text{SnO}_2(\text{s}) \rightarrow (\text{SnO})_n(\text{g})$	71 ± 2 (n=1; 298°K)
	75 ± 3 (n=2; 298°K)
	83 ± 10 (n=3; 298°K)

$n/2\text{Sn(s)} \rightarrow n/2\text{SnO}$	$(\text{SnO})_n(\text{g})$	89	± 15	($n=4; 298^\circ\text{K}$)
		105	± 20	($n=5; 298^\circ\text{K}$)
		106	± 25	($n=6; 298^\circ\text{K}$)
$\text{SnO(g)} \rightarrow \text{Sn(g)} + \text{O(g)}$		128.5	± 3	
$n\text{PbO(s)} \rightarrow (\text{PbO})_n(\text{g})$	$n=1-4$			
$\text{SiS(s)} \rightarrow \text{SiS(g)}$		63	± 3	(298°K)
$\text{SiS}_2(\text{s}) \rightarrow \text{SiS(g)} + 1/2\text{S}_2(\text{g})$		102	± 3	(298°K)
$\text{SiS}_2(\text{s}) \rightarrow \text{SiS}_2(\text{g})$		70	± 3	(298°K)
$\text{SiS(s)} \rightarrow \text{Si(s)} + \text{S(s)}$		38	± 3	(298°K)
$\text{SiS}_2(\text{s}) \rightarrow \text{Si(s)} + 2\text{S(s)}$		60	± 3	(298°K)
$\text{GeS(s)} \rightarrow \text{GeS(g)}$		38.7	± 0.6	(298°K)
$\text{GeS(g)} \rightarrow \text{Ge(g)} + \text{S(g)}$		134.1	± 2.0	
$\text{SnS(s)} \rightarrow \text{SnS(g)}$		52.6	± 1.6	(298°K) 19
$2\text{SnS(s)} \rightarrow \text{Sn}_2\text{S}_2(\text{g})$		56.5	± 5.0	(298°K)
$\text{SnS(g)} \rightarrow \text{Sn(g)} + \text{S(g)}$		110.1	± 3.0	
$\text{PbS(s)} \rightarrow \text{PbS(g)}$		55.7	± 1.6	(298°K) 19
$2\text{PbS(s)} \rightarrow \text{Pb}_2\text{S}_2(\text{g})$		66.6	± 5.0	(298°K)
$\text{PbS(g)} \rightarrow \text{Pb(g)} + \text{S(g)}$		79.1	± 2.8	
$\text{SnPbS}_2(\text{g}) \rightarrow \text{SnS(g)} + \text{PbS(g)}$		46.5	± 5.0	(298°K) 19
$\text{SnSe(s)} \rightarrow \text{SnSe(g)}$		47.5	± 3.0	(298°K)
$2\text{SnSe(s)} \rightarrow \text{Sn}_2\text{Se}_2(\text{g})$		47.9	± 5.0	(298°K)
$\text{SnSe(g)} \rightarrow \text{Sn(g)} + \text{Se(g)}$		95.0	± 4.0	
$\text{SnSe(s)} \rightarrow \text{Sn(s)} + \text{Se(s)}$		15.6	± 3.0	(298°K)

$\text{SnTe(s)} \rightarrow \text{SnTe(g)}$	$48.3 \pm 3.0 \text{ (298}^\circ\text{K)}$
$\text{SnTe(g)} \rightarrow \text{Sn(g)} + \text{Te(g)}$	80.9 ± 4.0
$\text{SnTe(s)} \rightarrow \text{Sn(s)} + \text{Te(s)}$	$11.0 \pm 3.0 \text{ (298}^\circ\text{K)}$

9. Relative Ionization Cross Sections^(8,9) from Double Oven Experiments with ZnSe (R. Colin, D. Detry, P. Goldfinger and M. Jeunehomme).

$$\sigma_{\text{Se}_2} / \sigma_{\text{Se}} / \sigma_{\text{Zn}} = 2.3/1/0.7 \quad (\pm 20\%) \text{ (24 eV)}$$

$$\sigma_{\text{Se}_2} / \sigma_{\text{Se}} / \sigma_{\text{Zn}} = 1.5/1/0.5 \quad (\pm 20\%) \text{ (70 eV)}$$

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